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A coarse-grained model for PETN crystals

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Abstract

Using the energetic material Pentaerythritol Tetranitrate (PETN) as a specific example of molecular crystal, we describe the development of a simple coarse-graining procedure by grouping several atoms or whole functional groups into single charge-neutral beads. As compared to fully atomistic calculations the coarse-grained model speeds up simulations by more than two orders of magnitude. Yet, by adjusting only two parameters in the coarse-grained interaction, the model accurately predicts the lattice constants, sublimation energy, pressure-volume curve up to P=10 GPa, and energetically the most stable facets. Computed surface and desorption energies, bulk modulus, and equilibrium morphology are reported as well.

Molecular crystals are becoming increasingly important in numerous applications ranging from drugs, pigments, agrochemicals, dyes, optoelectronic materials, and energetic materials used in detonation devices. Better utilization of such materials warrants a good understanding of the morphological properties of the crystals, as well as the response of exposed surfaces to external factors like temperature, impurities, solvent, and so on. With the availability of sophisticated inter-atomic interactions or force fields, parameterized primarily for organic molecules, it is becoming increasingly possible to study the surface kinetics and the morphological evolution of such materials at the atomic level via classical molecular mechanics [1]. However, typical molecules in such materials are uncharged and non-polar, and all the important dynamics is governed by weak inter-molecular interactions of short spatial range, while a significant part of atomistic molecular dynamics (MD) gets consumed in computing both intra-molecular and Coulombic energies and forces. One way to overcome this inefficiency is to coarse-grain a group of atoms into single charge-neutral "beads". The resulting decrease in the intra-molecular degrees of freedom and the absence of long-ranged electrostatics can significantly increase computational speed, while fewer inter-molecular interaction parameters can make it easier to fit select experimental parameters of interest for specific materials systems.

In this Letter we consider the energetic material Pentaerythritol Tetranitrate (PETN), and develop a simple coarse-grained interaction potential for use in MD or Monte Carlo simulations. As compared with fully atomistic calculations the coarse-grained potential is found to be more than 100 times faster. The fitting of a single length and a single energy term in the nonbond interaction yields not only accurate lattice constants, but several other properties, including sublimation energy, and pressure-volume (P-V) curve with excellent accuracy as compared to room-temperature experimental measurements. Additional quantities, i.e., dominant facets in the equilibrium morphology are also in agreement with existing experimental literature.

Fig. 1 displays the fully atomistic structure for both PETN molecule and crystalline unit cell [2] along with their coarse-grained representations. The experimental structure is body-centered-tetragonal (i.e., $a = b \neq c$, and $\alpha = \beta = \gamma = 90^{o}$). In the coarse-grained model each of the four NO_2 groups are lumped into a pendent *"B"*-bead, while the remaining atoms are grouped into a central "*A*"-bead. Even without any imposed symmetry constraints such a coarse-grained crystal, upon energy minimization (with a coarse-

grained interaction potential described below), relaxes into a configuration with body-centered-tetragonal symmetry. In other words, although our initially constructed coarse-grained crystal is not constrained to any specific symmetry, the relaxed structure conforms to the symmetry: $a = b \neq c$, and $\alpha = \beta = \gamma = 90^{o}$ [3]. As for interactions between the coarse-grained beads, only a minimal set is considered: (1) the intramolecular A-B bond interaction, chosen to be of the harmonic form: $E_{bond}(r_{AB}) = K_{bond}(r_{AB} - b_{AB}^{0})^{2}$; and (2) the B-B nonbond interaction, chosen to be in the 12-6 Lennard-Jones form $E_{vdw}(r_{BB}) = D_{BB}\{(\sigma_{BB}/r_{BB})^{12} - 2(\sigma_{BB}/r_{BB})^{6}\}$. Note that this later interaction is operative between both intra-molecular and inter-molecular B-beads, i.e., the 1-3 interactions are explicitly included. The inter-molecular interactions, represented solely by the B-B nonbond term govern most physical properties of interest for this system (vibrational properties were not of interest in this study). With only two nonbond parameters D_{BB} and σ_{BB} at our disposal, we could aim at accurately fitting two experimental quantities. With the room-temperature lattice constant *a* (9.38 Å) [2] and the room-temperature heat of sublimation (35.9 kcal/mol) [4] as these two fitting quantities we obtain D_{BB} = 1.38 kcal/mol and σ_{BB} = 4.84 Å. The bond interaction parameters K_{bond} and b_{AB}^{0} are assigned generic values of 20.0 kcal/mol and 2.6 Å respectively [5]. All other interactions, including the B-A-B angle term, as well as inter-molecular A-A and A-B interactions are neglected.

Table 1 lists the room-temperature values of the lattice constants, crystal density, bulk modulus, sublimation energy, and four points on the pressure-volume (P-V) curve as computed by the coarse-grained model described above, and compares with the corresponding experimental values and the values computed by fully atomistic calculations using a state-of-the-art force field COMPASS [6]. Finite-temperature quantities are obtained by performing NPT dynamics on a 6x6x6 supercell of the basic unit cell (512 coarse-grained molecules), and averaging over a simulation time of 100 ps (following an initial equilibration run of 50 ps). The Nosé-Hoover thermostat [7], Parrinello-Rahman barostat [8], a time-step of 0.001 ps, and nonbond-interaction-cutoff of 20 Å are employed in the NPT simulations. The heat of sublimation is computed by taking the difference of the average total energy of the 6x6x6 crystal normalized per molecule from the average total energy of an isolated coarse-grained molecule over an NVE dynamics run. The bulk modulus is obtained by fitting the low-P (< 0.5 GPa) part of the P-V curve to the

Murnaghan equation of state [9]. It is interesting to note that by adjusting only two parameters in the coarse-grained interaction we obtain accurate values for all lattice constants, the sublimation energy, and even the P-V curve up to P=10 GPa, as compared with room-temperature experimental data. Compared to experiment, the coarse-grained results are as good as or even better than fully atomistic COMPASS results. Only the room-temperature bulk modulus is underestimated by ~15-20 %. However, it should be noted that even the experimental value of bulk modulus is a highly sensitive function of the low-pressure (< 0.5 GPa) P-V data. Comparing the room-temperature results of Table 1 with the T = 0 results [10] we note that some of the quantities (most notably the bulk modulus) can display dramatic temperature dependence. Therefore, one should exert great caution when trying to fit calculated results at T = 0 to finite-temperature experimental observations, or when trying to compute quantities characterizing temperature-driven phenomena, e.g., thermal expansion coefficients, or melting point.

Table 2 lists the computed surface energies for the important low-index surfaces of PETN. Due to the unavailability of these energies in the experimental literature, we compare coarse-grained values with those of COMPASS. For simplicity and the ease of comparison we compute the surface energies at T = 0 (i.e. energy minimization) using the room-temperature experimental lattice ($a = b = 9.38$ Å, $c = 6.71$ Å). Wulff construction [11, 12] with the surface energies is then used to compute the equilibrium morphology [13] (Fig. 2). Experimental morphologies are known to primarily expose the {110} and the {101} facets [14], with the ratio between the areas of the facets displaying a range of variation. Both the coarse-grained and the COMPASS morphologies primarily expose the {110} and {101} facets, in agreement with experimental observations. However, both the computed morphologies expose small amounts of a few other facets as well, i.e, {100}, {001}, and {211} facets. Although the overall agreement between the coarse-grained and COMPASS surface energies is quite satisfactory, one should note the discrepancy in the energetics of the {001} face, leading to its prominent presence in the coarse-grained morphology.

Finally, with the aim of explaining recent experimental data on the evolution of crystal size and surface features as a function of temperature, we compute the desorption energies (at T = 0) of various molecular sites on the most exposed facet of PETN crystallites, i.e., the {110} family of planes. More specifically, we look at a molecule on the top of a defect-free flat surface, a molecule *in* the top layer of a flat surface, and

molecules on two different types of steps, i.e., one running along the <001> direction, and the other running along the <1 $\bar{1}$ 0> direction. Along the <001> steps, the PETN molecules are arranged in a straight line. For such steps we compute the desorption energy of a molecule belonging to a straight step, and that of a molecule at a step-kink (i.e. corner). The <1 $\bar{1}$ 0> steps, on the other hand, have a zigzag arrangement of molecules, and each site is almost like a kink. Results listed in Table 3 show that: (1) ad-molecules will easily desorb from flat surfaces at room temperature, unless they quickly diffuse to the nearest step (computed diffusion barrier is low, ~ 5-7 kcal/mol); (2) the desorption energy of a kink site is remarkably similar to the sublimation energy (both at T=0 [10] and at T=300K) both for our coarse-grained model and COMPASS, a clear indication of little surface relaxation; (3) there is a 6 kcal/mol difference in the pit-formation energy computed by the coarse-grained model and COMPASS, which could be traced back to the difference in the computed sublimation energies (see [10] and Table 1). Arrhenius fits to limited atomic force microscope (AFM) data suggest a pit-nucleation-energy in the range of 55-70 kcal/mol, which encompasses both the coarse-grained and the COMPASS values. More accurate measurements are necessary for a finer resolution of the energy.

In summary, we demonstrate that for crystals of uncharged non-polar molecules like PETN, it is possible to reproduce a large number of structural, energetic, and thermodynamic properties using only a few parameters describing nonbond interactions of *groups* of atoms. These simplifications not only speed up calculations by more than two orders of magnitude as compared to fully atomistic calculations, but also expose the truly important interaction parameters governing the system properties. The resulting speed and accuracy should enable detailed exploration of kinetic, thermodynamic, and growth properties of such crystallites both from the melt as well as in the vapor phase.

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10. For reference, we list here some computed values at T = 0 (i.e. by performing energy minimization rather than MD). The symbols are defined in Table 1. **Coarse-grained model**: $a = b = 9.27$ Å, $c = 6.59$ Å; $\rho_{crystal} = 1.85$ g/cc; $\Delta E_{sublimation} = 39.9$ kcal/mol; $B = 11.8$ GPa. **COMPASS**: $a = b = 9.16$ Å, $c = 6.62$ Å; $\rho_{crystal} = 1.89$ g/cc; $\Delta E_{sublimation} = 43.6$ kcal/mol; $B = 13.7$ GPa.

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Table 1. Important structural, energetic, and thermodynamic quantities of PETN: comparison between coarse-grained, fully atomistic (COMPASS), and experimental values (appropriate references indicated). All quantities are computed/measured at room temperature (T=300K). See [10] for computed results at T=0.

Property	Coarse-grained	COMPASS	Experiment
Lattice constant $a=b$ (Å)	9.38	9.35	9.38 [2]
Lattice constant c (Å)	6.70	6.67	6.71 [2]
α, β, γ	90^o	90^o	90^o [2]
Crystal Density $\rho_{crystal}$ (g/cc)	1.78	1.80	1.78 [2]
Bulk Modulus B (GPa)	7.0	8.1	8.3 - 9.1 [15, 16]
Sublimation Energy $\Delta E_{sublimation}$ (kcal/mol)	36.0	40.5	35.9 [4]
Volume strain (P=1 GPa)	0.07	0.06	0.07 [16]
Volume strain (P=2 GPa)	0.11	0.10	0.11 [16]
Volume strain (P=5 GPa)	0.18	0.17	0.18 [16]
Volume strain (P=10 GPa)	0.25	0.23	0.25 [16]

Table 2. Surface energies (at T=0) of PETN for most stable low-index planes: comparison between coarse-grained and fully atomistic (COMPASS) results. Corresponding Equilibrium morphologies are shown in Fig. 2.

Surface		{110}	{101}	{100}	{001}	{111}	{210}	{201}	{211}
Surface Energy (kcal/mol/Å^2)	Coarse-grained	0.215	0.257	0.257	0.262	0.274	0.251	0.274	0.269
	COMPASS	0.210	0.273	0.275	0.331	0.299	0.261	0.299	0.279

Table 3. Desorption energies of various sites on (110) surface (at T=0) – comparison between coarse-grained and COMPASS calculations. All steps are of single-molecular height.

Desorbing species [on the (110) surface]	Desorption Energy (kcal/mol)	
	Coarse-grained	COMPASS
Ad-molecule *on* a flat surface	20.0	19.2
Molecule *in the top layer* of a flat surface*	59.6	65.5
Molecule *in a straight* <001> step†	47.3	48.6
Molecule at a *kink* of <001> step**	39.9	43.8
Outer molecule *in a* <1 $\bar{1}$ 0> step‡	40.2	43.4

*Removal of such a molecule initiates the formation of a hole or pit. Therefore, such desorption energy could be interpreted as a pit-formation energy.

†Such desorption leads to the formation of two nearest-neighbor kinks.

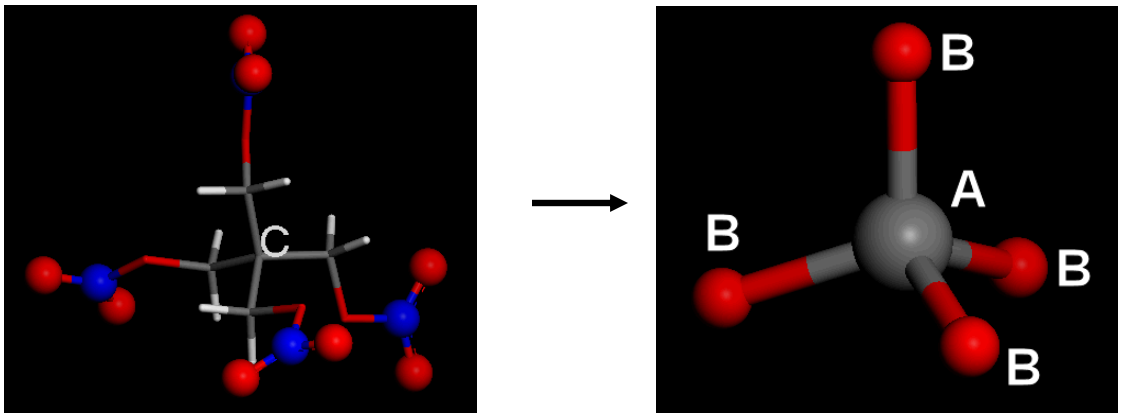
**Such a kink-molecule has exactly half the neighbors as compared to a molecule in the bulk crystal. Therefore, under small surface relaxation (as is the case here), such desorption energy is equal to the sublimation energy [10]. We have verified this also for T=300K.

‡The <1 $\bar{1}$ 0> step on the (110) surface is molecularly zigzag. Thus the position of the outer molecules is almost like a kink site.

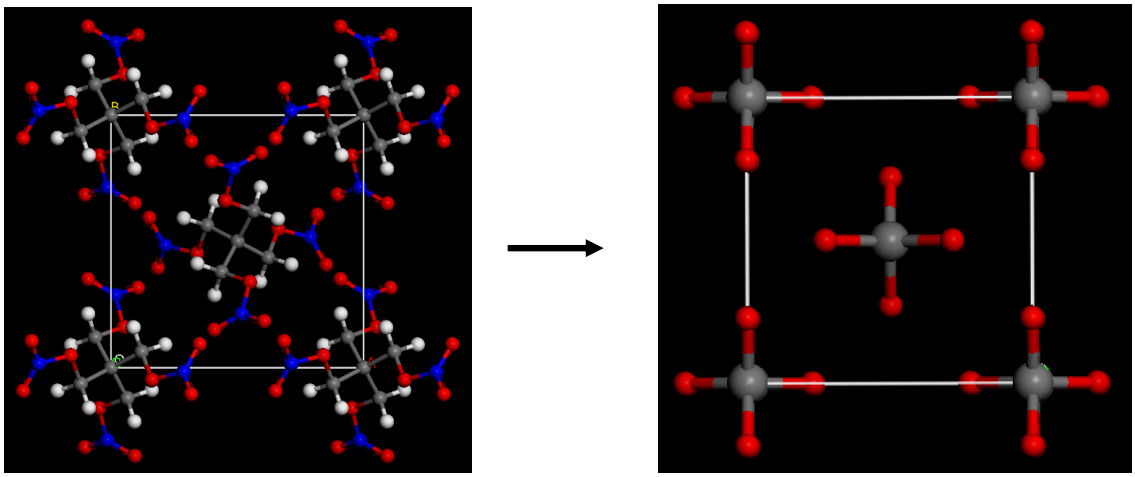
Figure captions:

1. Schematic showing the coarse-graining procedure: (a) Coarse-graining of a PETN molecule, where the central C atom and its four C-neighbors, the associated H-atoms, and the bonded inner O atoms (i.e. all atoms shown in stick representation) are coarse-grained into the central "A"-bead, while each NO_2 group (in ball & stick representation) is coarse-grained into a pendent "B"-bead; (b) Coarse-grained PETN crystal.

2. Equilibrium morphologies of PETN obtained from the surface energies of Table 2. (a) Coarse-grained equilibrium morphology; (b) COMPASS equilibrium morphology. Predominantly exposed facets are indicated by their Miller indices.

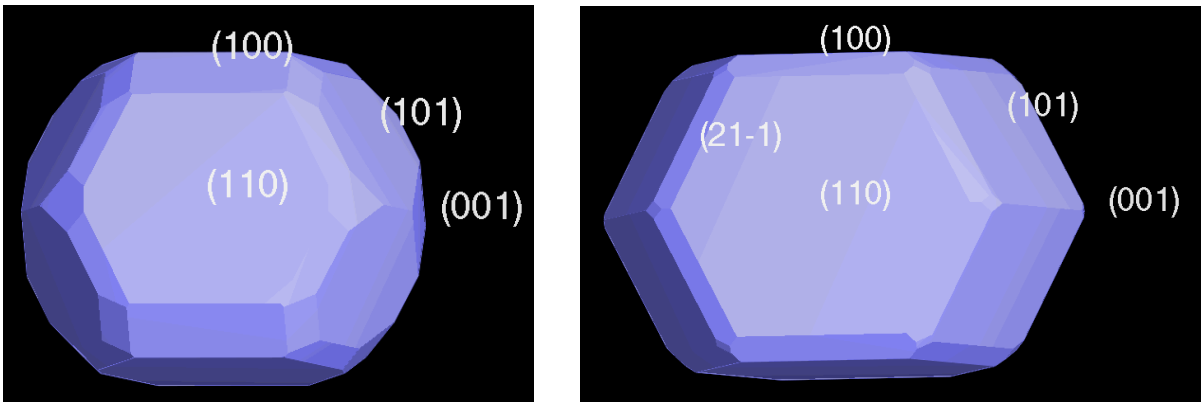


(a)



(b)

Figure 1



(a) (b)

Figure 2